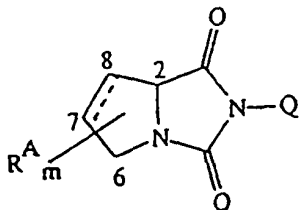




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<p>(21) International Application Number: PCT/EP93/02413</p> <p>(22) International Filing Date: 6 September 1993 (06.09.93)</p> <p>(30) Priority data: 07/942,800 10 September 1992 (10.09.92) US</p> <p>(71) Applicant (for all designated States except US): DEGUSSA AKTIENGESELLSCHAFT [DE/DE]; Weißfrauenstraße 9, D-60311 Frankfurt am Main (DE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : SCHÄFER, Matthias [DE/DE]; Sonnenstraße 2, D-63808 Haibach (DE). DRAUZ, Karlheinz [DE/DE]; Zur Marienruhe 13, D-63579 Freigericht (DE). FEIT, Dieter [DE/DE]; Siedlungsstraße 1, D-63607 Wächtersbach (DE). AMUTI, Kofi, Sam [GH/US]; 5412 Valley Green Drive, Wilmington, DE 19808 (US).</p>		<p>(74) Agent: V. BIEDERSEE, Heidereich; Degussa Aktiengesellschaft, Patentabteilung, Postfach 13 45, Rodenbacher Chaussee 4, D-63403 Hanau (DE).</p> <p>(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>

(54) Title: BICYCLIC IMIDES AS HERBICIDES



(I)

(57) Abstract

Bicyclic imides of formula (I), wherein the bond linking C-7 and C-8 may be single or double; m is 1-7; R^A can occupy one or more of the 2 or 6-8 positions and is independently selected from the group: hydroxy, halogen, CN, OR³, (C₁-C₄)alkyl, S(O)_nR³, COR³, C(O)SR³ and C(O)NR¹¹R¹²; and Q is a phenylic residue substituted with one or more inorganic and/or organic residues which can be substituted, interrupted and/or combined with the aromatic residue with one or more hetero atoms such as N, O or S, preferably at least in the 4' position. These compounds are made from aryl isocyanates of the general formula Q - N = C = O and proline carboxylic acids. The compounds are useful as herbicides.

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Bicyclic Imides as herbicides

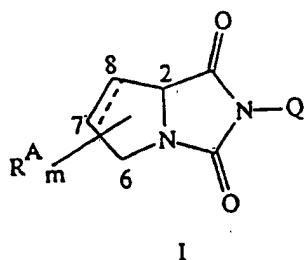
Description

This invention relates to novel bicyclic imides; a method for their preparation; and their use as herbicides.

It has already been disclosed that certain heterocyclic imides (see EP-A 272 594, EP-A 493 323, EP-B 0 070 389, EP-B 0 104 532) can be employed as herbicides.

Now novel bicyclic imides have been found that exhibit markedly better herbicidal activity with excellent selectivity.

The subject of the present invention therefore comprises compounds of formula I



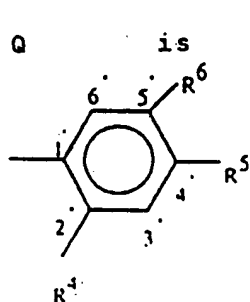
wherein

the bond linking C-7 and C-8 may be single or double;

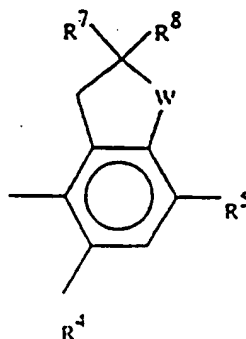
m is 1 - 7;

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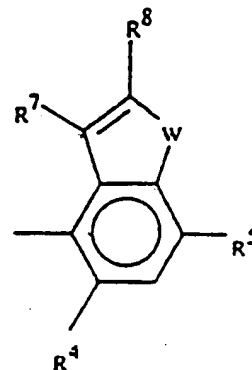
R^A can occupy one or more of the 2 or 6 - 8 positions and is independently selected from the group: hydroxy, halogen, CN, OR^3 , $(C_1-C_4)alkyl$, $S(O)_nR^3$, COR^3 , $C(O)SR^3$ and $C(O)NR^{11}R^{12}$;



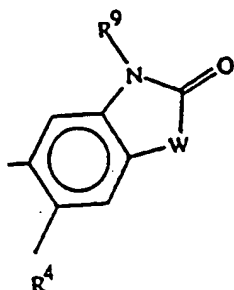
Q-1



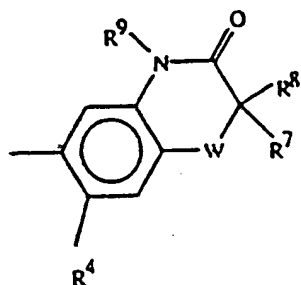
Q-2



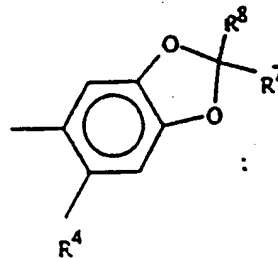
Q-3



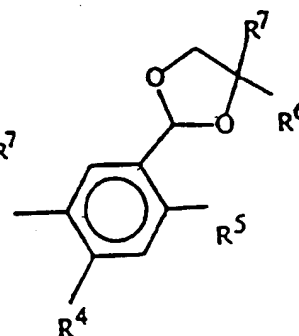
Q-4



Q-5



Q-6



Q-7

wherein

R^3 is $(C_1-C_8)alkyl$, $(C_3-C_8)cycloalkyl$,
 $(C_3-C_8)alkenyl$, $(C_3-C_8)alkynyl$, $(C_1-C_8)haloalkyl$,
 $(C_2-C_8)alkoxyalkyl$, $(C_2-C_4)carboxy alkyl$,
 $(C_3-C_8)alkoxycarbonylalkyl$,
 $(C_4-C_8)alkenyloxyalkyl$, $(C_4-C_8)alkynyloxyalkyl$,
 $(C_3-C_8)haloalkoxyalkyl$, $(C_3-C_8)trialkylsilyl$,
 $(C_3-C_8)cyanoalkyl$, $(C_3-C_8)haloalkenyl$,
 $(C_3-C_8)haloalkynyl$, $(C_2-C_8)alkylcarbonyl$,
 $(C_2-C_8)alkoxycarbonyl$, $(C_2-C_8)haloalkoxycarbonyl$,

$P(O)(OR^{17})_2$, $CHR^{16}P(O)(OR^{17})_2$ or $CHR^{16}P(S)(OR^{17})_2$, phenyl or benzyl optionally substituted with halogen, (C_1-C_3) alkyl, (C_1-C_3) haloalkyl or (C_1-C_4) alkoxy;

R^4 is hydrogen or halogen;

R^5 is (C_1-C_2) alkyl, (C_1-C_2) haloalkyl, OCH_3 , SCH_3 , $OCHF_2$, halogen, CN or NO_2 ;

R^6 is hydrogen, (C_1-C_8) alkyl, (C_1-C_8) haloalkyl, halogen, OR^{10} , $S(O)_n R^{10}$, COR^{10} , $C(O)SR^{10}$, $C(O)NR^{11}R^{12}$, CHO , $CH=CHCO_2R^{10}$, $CO_2N=CR^{13}R^{14}$, NO_2 , CN, $NHSO_2R^{15}$ or $NHSO_2NHR^{15}$;

R^7 and R^8 are independently hydrogen, (C_1-C_3) alkyl, (C_1-C_3) haloalkyl or halogen; when Q is Q-2 or Q-6, R^7 and R^8 together with the carbon to which they are attached may be $C=O$;

R^9 is (C_1-C_6) alkyl, (C_1-C_6) haloalkyl, (C_2-C_6) alkoxyalkyl, (C_3-C_6) alkenyl or (C_3-C_6) alkynyl;

R^{10} is (C_1-C_8) alkyl, (C_3-C_8) cycloalkyl, (C_3-C_8) alkenyl, (C_3-C_8) alkynyl, (C_1-C_8) haloalkyl, (C_2-C_8) alkoxyalkyl, (C_2-C_8) alkylthioalkyl, (C_2-C_8) alkylsulfinylalkyl, (C_2-C_8) alkylsulfonylalkyl, (C_3-C_8) alkoxyalkoxyalkyl, (C_4-C_8) cycloalkylalkyl, (C_2-C_4) carboxyalkyl, (C_3-C_8) alkoxycarbonylalkyl, (C_6-C_8) alkenyloxycarbonylalkyl, (C_6-C_8) alkynyloxycarbonylalkyl, (C_6-C_8) cycloalkoxyalkyl, (C_4-C_8) alkenyloxyalkyl, (C_4-C_8) alkynyloxyalkyl, (C_3-C_8) haloalkoxyalkyl, (C_4-C_8) haloalkenyloxyalkyl, (C_4-C_8) haloalkynyloxyalkyl, (C_6-C_8) cycloalkylthioalkyl, (C_4-C_8) alkenylthioalkyl, (C_4-C_8) alkynylthioalkyl,

...

(C₄-C₈)trialkylsilylalkyl, (C₃-C₈)cyanoalkyl,
 (C₃-C₈)halocycloalkyl, (C₃-C₈)haloalkenyl,
 (C₅-C₈)alkoxyalkenyl, (C₅-C₈)haloalkoxyalkenyl,
 (C₅-C₈)alkylthioalkenyl, (C₃-C₈)haloalkynyl,
 (C₅-C₈)alkoxyalkynyl, (C₅-C₈)haloalkoxyalkynyl,
 (C₅-C₈)alkylthioalkynyl, (C₂-C₈)alkylcarbonyl,
 CHR¹⁶COR¹⁷, CHR¹⁶P(O)(OR¹⁷)₂, P(O)(OR¹⁷)₂,
 CHR¹⁶P(S)(OR¹⁷)₂, CHR¹⁶C(O)NR¹¹R¹², CHR¹⁶C(O)NH₂,
 (C₁-C₄)alkyl substituted with phenoxy or benzyloxy
 optionally substituted with halogen, (C₁-C₃)alkyl
 or (C₁-C₃)haloalkyl; benzyl optionally substituted
 with halogen, (C₁-C₃)alkyl or (C₁-C₃)haloalkyl; or
 phenyl and pyridyl optionally substituted with
 halogen, (C₁-C₃)alkyl, (C₁-C₃)haloalkyl or
 (C₁-C₄)alkoxy;

R¹¹ and R¹³ are independently hydrogen or
 (C₁-C₄)alkyl;

R¹² and R¹⁴ are independently (C₁-C₄)alkyl, or
 phenyl optionally substituted with halogen,
 (C₁-C₃)alkyl, (C₁-C₃)haloalkyl or (C₁-C₄)alkoxy;

R¹¹ and R¹² may be taken together as -(CH₂)₅-,
 -(CH₂)₄- or -CH₂CH₂OCH₂CH₂-, in which
 optionally one or more H-atoms may be replaced by
 (C₁-C₃)alkyl, phenyl or benzyl;

R¹³ and R¹⁴ may be taken together with the carbon
 to which they are attached to form
 (C₃-C₈)cycloalkyl;

R¹⁵ is (C₁-C₄)alkyl or (C₁-C₄)haloalkyl;

R¹⁶ is hydrogen or (C₁-C₃)alkyl;

R¹⁷ is (C₁-C₆)alkyl, (C₃-C₆)alkenyl or (C₃-C₆)alkynyl;

W is O or S;

n is 0, 1 or 2;

provided that

...

when Q is not fused to a ring bridging the 5'- and 6'-position and C-7 and C-8 are linked by a single bond, then at least one R^A is other than hydroxy, halogen, (C₁-C₄)alkyl and (C₁-C₄)alkoxy.

The subject of the present invention comprises further bicyclic imides selected from the group consisting of 4-[4'-chloro-2'-fluoro-5'-(prop-2-ynyloxy)phenyl]-3,5-dioxo-7-fluoro-1,4-diazabicyclo-[3.3.0]octane, 4-[4'-chloro-2'-fluoro-5'-(1-methyl-prop-2-ynyloxy)phenyl]-3,5-dioxo-7-fluoro-1,4-diazabicyclo[3.3.0]octane, 4-[4'-chloro-2'-fluoro-5'-(2-propynyloxy)phenyl]-3,5-dioxo-7-chloro-1,4-diazabicyclo[3.3.0]octane, 4-[4'-chloro-2'-fluoro-5'-(1-methyl-ethoxy)phenyl]-3,5-dioxo-7,7-difluoro-1,4-diazabicyclo[3.3.0]octane and stereoisomers thereof.

In the above definitions, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl", includes straight chain or branched alkyl, e. g., methyl, ethyl, n-propyl, isopropyl or the different butyl isomers. Alkoxy includes e. g. methoxy, ethoxy, n-propyloxy, isopropyloxy and the different butoxy isomers. Alkenyl includes straight chain or branched alkenes, e. g., 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl isomers. Cycloalkyl includes e. g. cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The term "halogen", either alone or in compound words such as "haloalkyl", means fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl" said alkyl may be partially or fully

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substituted with halogen atoms, which may be the same or different. Examples of haloalkyl include $\text{CH}_2\text{CH}_2\text{F}$, CF_2CF_3 and CH_2CHFCl .

More preferred are compounds of formula I having at least one of the following specifications

- R^3 is preferred (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl, (C_3-C_6) alkenyl, (C_3-C_6) alkynyl, (C_1-C_4) haloalkyl, (C_2-C_4) alkoxyalkyl, (C_2-C_4) carboxyalkyl, (C_3-C_6) alkoxycarbonylalkyl, (C_4-C_6) alkenyloxyalkyl, (C_4-C_6) alkynyloxyalkyl, (C_3-C_6) haloalkoxyalkyl, (C_3-C_6) trialkylsilyl, (C_3-C_6) cyanoalkyl, (C_3-C_6) haloalkenyl, (C_3-C_6) haloalkynyl, (C_2-C_6) alkyl carbonyl, $\text{P}(\text{O})(\text{OR}^{17})_2$, (C_2-C_6) alkoxycarbonyl, (C_2-C_6) haloalkoxycarbonyl, $\text{CHR}^{16}\text{P}(\text{O})(\text{OR}^{17})_2$ or $\text{CHR}^{16}\text{P}(\text{S})(\text{OR}^{17})_2$, phenyl or benzyl optionally substituted with halogen, (C_1-C_3) alkyl, (C_1-C_3) haloalkyl or (C_1-C_4) alkoxy;
- R^5 is halogen or CN;
- R^6 is hydrogen, (C_1-C_4) alkyl, (C_1-C_4) haloalkyl, halogen, OR^{10} , $\text{S}(\text{O})_n\text{R}^{10}$, COR^{10} , CO_2R^{10} , $\text{C}(\text{O})\text{SR}^{10}$, $\text{C}(\text{O})\text{NR}^{11}\text{R}^{12}$, $\text{CH}=\text{CHCO}_2\text{R}^{10}$, $\text{CO}_2\text{N}=\text{CR}^{13}\text{R}^{14}$, $\text{NHSO}_2\text{R}^{15}$ or $\text{NHSO}_2\text{NHR}^{15}$;
- R^7 and R^8 are independently hydrogen, (C_1-C_3) alkyl or (C_1-C_3) haloalkyl; when Q is Q-2 or Q-6, R^7 and R^8 together with the carbon to which they are attached may be $\text{C}=\text{O}$;
- R^9 is (C_1-C_4) alkyl, (C_1-C_4) haloalkyl, (C_2-C_4) alkoxyalkyl, (C_3-C_6) alkenyl or (C_3-C_6) alkynyl;

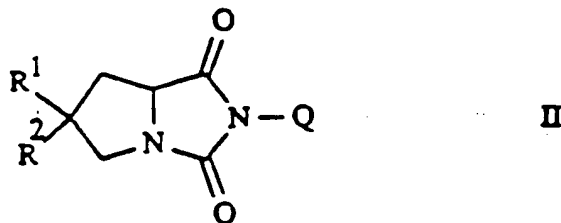
R^{10} is (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl,
 (C_3-C_6) alkenyl, (C_3-C_6) alkynyl, (C_1-C_4) haloalkyl,
 (C_2-C_4) alkoxyalkyl, (C_2-C_4) alkylthioalkyl,
 (C_2-C_4) alkylsulfinylalkyl,
 (C_2-C_4) alkylsulfonylalkyl,
 (C_3-C_6) alkoxyalkoxyalkyl, (C_4-C_8) cycloalkylalkyl,
 (C_2-C_4) carboxyalkyl, (C_3-C_6) alkoxycarbonylalkyl,
 (C_6-C_8) alkenyloxy carbonylalkyl,
 (C_6-C_8) alkynyloxy carbonylalkyl,
 (C_6-C_8) cycloalkoxyalkyl, (C_4-C_6) alkenyloxyalkyl,
 (C_4-C_6) alkynyloxyalkyl, (C_3-C_6) haloalkoxyalkyl,
 (C_4-C_8) haloalkenyloxyalkyl,
 (C_4-C_6) haloalkynyloxyalkyl,
 (C_6-C_8) cycloalkylthioalkyl,
 (C_4-C_6) alkenylthioalkyl, (C_4-C_6) alkynylthioalkyl,
 (C_4-C_8) trialkylsilylalkyl, (C_3-C_4) cyanoalkyl,
 (C_3-C_6) halocycloalkyl, (C_3-C_6) haloalkenyl,
 (C_5-C_6) alkoxyalkenyl, (C_5-C_6) haloalkoxyalkenyl,
 (C_5-C_6) alkylthioalkenyl, (C_3-C_6) haloalkynyl,
 (C_5-C_6) alkoxyalkynyl, (C_5-C_6) haloalkoxyalkynyl,
 (C_5-C_6) alkylthioalkynyl, (C_2-C_4) alkyl carbonyl,
 $CHR^{16}COR^{17}$, $CHR^{16}P(O)(OR^{17})_2$, $P(O)(OR^{17})_2$,
 $CHR^{16}P(S)(OR^{17})_2$, $CHR^{16}C(O)NR^{11}R^{12}$, $CHR^{16}C(O)NH_2$,
 (C_1-C_2) alkyl substituted with phenoxy or benzyloxy
optionally substituted with halogen, (C_1-C_3) alkyl
or (C_1-C_3) haloalkyl; benzyl optionally substituted
with halogen, (C_1-C_2) alkyl or (C_1-C_2) haloalkyl; or
phenyl and pyridyl optionally substituted with
halogen, (C_1-C_3) alkyl, (C_1-C_3) haloalkyl or
 (C_1-C_4) alkoxy;
 R^{12} and R^{14} are independently (C_1-C_2) alkyl, phenyl
optionally substituted with halogen, (C_1-C_2) alkyl,
 (C_1-C_2) haloalkyl or (C_1-C_2) alkoxy;

...

R^{11} and R^{12} may be taken together as $-(CH_2)_5-$, $-(CH_2)_4-$ or $-CH_2CH_2OCH_2CH_2-$, each ring optionally substituted with (C_1-C_2) alkyl, phenyl or benzyl;
 R^{13} and R^{14} may be taken together with the carbon to which they are attached to form (C_3-C_6) cycloalkyl;
 R^{17} is (C_1-C_4) alkyl, (C_3-C_6) alkenyl or (C_3-C_6) alkynyl.

Compounds having a substituted proline residue, particularly in 7-position, exhibit a beneficial effect on undesired plants, preferred are fluoro, bromo or chloro.

Particularly preferred method of use employs compounds of formula II



in which

R^1 is hydrogen, halogen, (C_1-C_4) alkyl, OR^3 , $S(O)_nR^3$, COR^3 , CO_2R^3 , $C(O)SR^3$, $C(O)NR^{11}R^{12}$ or CN;
 R^2 is halogen, (C_1-C_4) alkyl, OR^3 , $S(O)_nR^3$, COR^3 , CO_2R^3 , $C(O)SR^3$, $C(O)NR^{11}R^{12}$ or CN.

Especially preferred method of use employs compounds of formula II in which at least one of $R^1 - R^3$ has the meaning

- R^1 = hydrogen or (C_1-C_4) alkyl;
 R^2 = fluoro, chloro, bromo, OR^3 , $S(O)_nR^3$,
 CO_2R^3 , $C(O)NR^{11}R^{12}$ or CN;
 R^3 = (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl, (C_3-C_6) alkenyl,
 (C_3-C_6) alkynyl, (C_1-C_4) haloalkyl or
 (C_3-C_6) trialkylsilyl.

Most preferred method of use employs compounds of formula II with at least one of the following specifications

- R^1 = hydrogen,
 R^2 = fluoro, chloro, bromo or OR^3 ,
 R^3 = (C_1-C_2) alkyl, (C_1-C_2) haloalkyl,

and in Q

- R^4 is fluoro or chloro;
 R^5 is chloro;
 R^6 is OR^{10} , CO_2R^{10} , $NHSO_2R^{10}$ or SR^{10} ;
 R^7 is hydrogen;
 R^8 is hydrogen or methyl;
 R^9 is (C_3-C_4) alkenyl or (C_3-C_4) alkynyl;
 R^{10} is (C_1-C_4) alkyl, (C_3-C_6) cycloalkyl,
 (C_3-C_6) alkenyl, (C_3-C_4) alkynyl, (C_1-C_3) haloalkyl,
 (C_2-C_4) alkoxyalkyl, (C_3-C_6) alkoxycarbonylalkyl,
 (C_6-C^8) alkenyloxycarbonylalkyl,
 (C^6-C^8) alkynyloxycarbonylalkyl or
 (C^1-C^2) carboxyalkyl.

If not otherwise specified the invention relates to both the individual possible stereoisomers of formula

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